

1054788



## PATENT SPECIFICATION

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Inventor: JAMES RONALD CHARLTON.

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## COMPLETE SPECIFICATION

### Improvements in and relating to the manufacture of Foamed Polyurethanes

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with the manufacture of foamed polyurethanes from polyether polyols and polyisocyanates, particularly, though not exclusively, by the so-called "one-shot" method; with the resulting polyurethane foams; and with shaped articles consisting of or comprising such polyurethane foams.

In the manufacture of flexible foamed polyurethanes from polyether polyols and polyisocyanate reactants by the one-shot method, in which foaming is effected either wholly or partly by carbon dioxide generation *in situ* in the reaction mixture as the result of using water as a co-reactant, efficient mixing of the reactants is very important. In practice the kind of high speed mixing head now available to polyurethane foam manufacturers permits a good degree of mixing to be achieved by purely physical dispersion. In the one-shot method it is, however, important to achieve the required homogeneous mixture of reactants as quickly as possible in order to keep in balance the several reactions which take place in a short interval of time to form a polyurethane of cellular (foamed) structure. The Applicants have now found that the molecular structure of the polyether polyol reactant is important in this respect and they have found that polyether polyols having a molecular structure providing a defined content and disposition of oxyethylene radicals and having free hydroxyl groups which are essentially secondary hydroxyl groups exhibit advantages when used for the manufacture of flexible foamed polyurethanes by the one-shot method, the result-

ing foamed polyurethanes having desirable open cell structures.

In this specification a foam having an open cell structure means a polyurethane foam which when cut in a plane parallel to the direction of rise shows substantially only (i.e. at least 80%) open cells. In the art the cell structure of a polyurethane foam is usually judged by eye from its appearance on cutting in the manner just indicated.

According to the present invention a process for the manufacture of a flexible polyurethane foam by reacting under foam-forming conditions an organic polyisocyanate reactant and an hydroxyl-containing reactant comprising or consisting of a polyether polyol which is a condensation product of an organic compound containing at least two replaceable hydrogen atoms in the molecule, for example, an organic polyhydroxy compound, with ethylene oxide and propylene oxide, said polyol having an hydroxyl equivalent weight of at least 700 and the oxyethylene radical content thereof (expressed as ethylene oxide) being between 5 and 25% by weight of the total oxyethylene and oxypropylene radical content thereof (expressed as total ethylene oxide and propylene oxide), wherein said oxyethylene radicals are non-terminal radicals whereby said polyether polyol contains essentially (i.e. at least 95% of the total hydroxyl groups) secondary hydroxyl groups in its molecular structure and said oxyethylene radicals are disturbed in a random manner in a portion of the molecular structure of said polyol as the result of preparing said polyol by reacting said organic compound containing replaceable hydrogen atoms with a mixture of ethylene oxide and propylene oxide to form an intermediate adduct which is then reacted with propylene oxide only to form the required polyether polyol. The present invention also includes the resulting flexible polyurethane foam.

Preferably said polyether polyol has an hydroxyl equivalent weight of at least 800,

e.g. at least 850 to 1000 and in general an hydroxyl equivalent weight of between 700 and 1800 can be mentioned, e.g. between 1000 and 1400; the term hydroxyl equivalent weight signifying the average molecular weight of the polyether polyol divided by the number of hydroxyl groups in the molecular structure of the polyether polyol. Preferably said polyether polyol has at least three hydroxyl groups per molecule, although polyether polyols with only two such hydroxyl groups are not excluded since such polyether polyols (which are of course diols) can also be used in the manufacture of flexible polyurethane foams e.g. in combination with other polyols, which can be polyether polyols, if desired containing combined phosphorus and/or chlorine in the molecule. A preferred oxyethylene radical content for said polyether polyol is between about 5 and 20%, advantageously between 8 and 15% and preferably between 10 and 14% e.g. about 12 to 13%, by weight of the total oxyethylene and oxypropylene radical content of said polyol.

The polyether polyol as defined above can be prepared by reacting said intermediate adduct with propylene oxide under conditions including the use of a catalyst such as an alkali metal catalyst, e.g. sodium or potassium hydroxide; or a sodium or potassium alkoxide e.g. the methoxide and an elevated temperature between 100 and 140°C, e.g. 110-120°C, to ensure the formation of secondary hydroxyl groups in the polyol product.

Preferably said polyether polyol is prepared by reacting a polyol, which can be a diol but is preferably an organic compound containing at least three hydroxyl groups in the molecule e.g. glycerol, with a mixture of ethylene oxide and propylene oxide, e.g. 6 to 50% by weight of ethylene oxide and 50 to 94% by weight of propylene oxide, to form said intermediate adduct, which adduct is then reacted with only propylene oxide. If desired an inert gas purge or other stripping operation can be employed to remove any unreacted oxides from said intermediate adduct, but this is not usually necessary. Preferably for convenience of operation said intermediate adduct is reacted with propylene oxide in the pressure vessel in which it is formed and conveniently in such case the supply of the mixed ethylene oxide/propylene oxide feed is simply changed to a propylene oxide feed when the molecular weight of the intermediate adduct is such that any unreacted ethylene oxide remaining in the reaction mixture after the change becomes used up in reaction sufficiently before the ultimately desired molecular weight of the polyether polyol product is reached to ensure that said polyether polyol product contains essentially only secondary hydroxyl groups and has the desired molecular structure defined above. In referring to a mixed ethylene oxide/propylene oxide feed, it

will be understood that said oxides can be supplied either separately or in prior admixture to the reactor in the desired relative amounts.

In accordance with the present invention a flexible foamed polyurethane having desirable open cell characteristics is prepared from an hydroxyl-containing reactant comprising or consisting of a polyether polyol as hereinbefore defined and an organic polyisocyanate reactant under any known or suitable foam-forming conditions. Preferably such a foamed polyurethane is formed by the one-shot method in which foam formation results either wholly or partly from the use of water as a co-reactant. Usually foam formation may be achieved substantially wholly as the result of carbon dioxide generation *in situ* in the reaction mixture from water, but the use of an auxiliary foaming agent comprising a volatile liquid e.g. a halogenated hydrocarbon such as those sold under the trade names "Freon"; "Arcton"; "Genetron" and "Isceon" in conjunction with water is not excluded. The words "Freon"; "Arcton" and "Isceon" are Registered Trade Marks.

Preferably said organic polyisocyanate comprises or consists of a di-isocyanate e.g. toluene diisocyanate, (which is available commercially as mixtures of the 2:4 and 2:6 isomers e.g. an 80% 2:4/20% 2:6 mixture and a 65% 2:4/35% 2:6 mixture), although other polyisocyanates as described for example in our U.K. Application No. 33,834/60 (Serial No. 967,441) can also be used. Since the polyether polyols can be used, in accordance with the present invention, for the manufacture of flexible polyurethane foams by any known as suitable method, a detailed description of polyurethane foam manufacture *per se* is considered to be unnecessary in this specification.

The polyether polyols for use in the present invention can be prepared from a wide variety of organic compounds containing at least two replaceable hydrogen atoms in the molecule, for example organic compounds in which at least two hydrogen atoms are activated by oxygen atoms as in a hydroxyl group, a phenol group and a carboxylic acid group; or by a basic nitrogen atom as in an amine group, a hydrazine group, an imine group, an amide group, a guanidine group, a sulphonamide group, an urea group and a thiourea group; or by a sulphur atom as in a mercaptan, a thiophenol and a thiocarboxylic acid. Examples of such compounds are glycerol, ethylene glycol, 1,2-propylene glycol, butanediol, trimethylol propane, hexane triol, oxalic acid, triethanolamine, aniline, resorcinol, tri-isopropanolamine, pentaerythritol, sucrose, sorbitol, ethylene diamine and acetamide. Polyether polyols derived from glycerol are at present preferred.

The present invention is further described and illustrated by the following examples in which Examples II and III describe the pre-

paration of polyether polyols *per se*:—

#### EXAMPLE I

5 A pressure vessel was charged with 7.5 pounds of glycerol in which 0.9 pounds of flaked potassium hydroxide was dissolved as catalyst. The contents of the vessel were then heated to 115°C and 172 pounds of a mixture of 24% wt. ethylene oxide and 76% wt. propylene oxide was fed in until an intermediate adduct having a molecular weight of about 1800 had been formed. The oxide feed was then changed to propylene oxide alone and the reaction continued by the addition of 166 pounds of propylene oxide until a polyol

product having a molecular weight of 3540 had been produced. This polyether polyol product had an hydroxyl equivalent of 1180 and it contained about 12.0% of combined ethylene oxide. The polyether polyol product contained only secondary hydroxyl groups in its molecular structure. 15 20

The polyether polyol was used for the manufacture of a foamed polyurethane by reaction with toluene di-isocyanate (80% 2:4 isomer content) in accordance with the following formulation, in which the words "Dabco" and "Nuocure" are Registered Trade Marks:— 25

Polyether polyol	100 parts by weight
Water	3 parts by weight
"Dabco" (triethylene diamine)	0.2 part by weight
"Nuocure" 28 (stannous octoate)	0.1 part by weight
Silicone oil L520	1.0 part by weight
TDI (80:20)	38.7 parts by weight

30 The polyurethane foam was made in a four component continuous machine having a total throughput of 2000 grams per minute.

It was found that manufacture of the foamed

polyurethane occurred satisfactorily to form a good flexible polyurethane foam of desirable characteristics as indicated by the following product properties:— 35

Density	37.5 grams/litre
Tensile strength	24 pounds per square inch (psi)
Elongation	360%
Compression strength (40% compression)	0.45 psi
Compression set (16 hours at 75% compression and 70°C)	7.5%
Rebound resilience	42%

40 By way of comparison a polyol made by condensing propylene oxide only with a tri-functional nucleating agent was substituted for the polyether polyol specified in the above formulation but it was found that foam collapse occurred at the order of catalyst concentration specified.

#### EXAMPLE II

45 A one ton batch of a polyether polyol in accordance with the present invention was made in the following manner. A pressure vessel was charged with 79 pounds of glycerol containing 8.35% by weight of flaked potassium hydroxide which had been dissolved therein by stirring under nitrogen at a tem-

perature not exceeding 80°C. The contents of the vessel were heated to 115°C and maintained at 115-120° C whilst 1450 pounds of a mixture of 24.4% by weight of ethylene oxide and 75.6% by weight of propylene oxide was fed to the vessel over a 5 hour period, the mixed oxides being fed in at a rate sufficient to maintain the pressure in the vessel below 50 pounds per square inch (gauge). 55 60 After 5 hours the reaction mixture comprised a condensation product having a molecular weight of about 1500 and the oxide feed was then changed to propylene oxide alone and a total of 1,464 pounds of propylene oxide was fed in over a 6 hour period. The reaction was then continued for a further 4 hours during 65

which time the residual oxide content of the reaction system dropped to 1% by weight (of propylene oxide). The resulting product was then vacuum stripped at 100-115°C, neutralised and vacuum dried to give a polyether polyol having a molecular weight of about 3000 and a hydroxyl value of 56.8 milligrams of KOH per gram. Neutralisation was effected by the addition of 60 pounds of "Puron" (the word "Puron" is a Registered Trade Mark), followed by 30 pounds of water after which the reaction product was stirred at 100°C for 2 hours.

### EXAMPLE III

A number of polyether polyols suitable for the manufacture of polyurethane foams in accordance with the present invention were made in the following manner. Potassium hydroxide was dissolved in glycerol by stirring under nitrogen at 70°C. A pressure vessel was charged with the glycerol containing catalyst and 12 litres of a mixture of ethylene oxide and propylene oxide was added. The resulting

reaction mixture was then heated to 115°C with stirring and, when reaction commenced, a mixture of ethylene oxide and propylene oxide was fed to the reaction vessel to maintain the pressure therein at 50 pounds per square inch (gauge). When sufficient oxide had been supplied to the vessel (i.e. initially and in the subsequent feed) to form a condensation product having a molecular weight of about one-half that of the desired end product, the oxide feed was changed to propylene oxide alone. The reaction was continued until the free oxide (propylene oxide) content of the reaction mixture was not more than 1% by weight, whereupon the product was neutralised with "Puron" (the word "Puron" is a Registered Trade Mark) and water and vacuum stripped as described in Example II, using about 2% by weight of "Puron" and 1% by weight of water. The particular conditions and the results obtained in a number of preparations in the manner described are indicated in the table below:—

		Polyether polyols				
		1	2	3	4	5
Glycerol	(pounds)	7.68	7.26	7.26	7.56	15.1
KOH	( " )	0.81	0.81	0.81	0.81	1.62
Mixed oxides	( " )	146.1	146.4	146.4	146.4	284.9
Propylene oxide	( " )	146.1	146.4	146.4	150	300
Reaction times:						
a) mixed oxides	(hours)	7.5	9.5	6.0	10.75	10.75
b) propylene oxide	( " )	5.5	5.75	5.5	8	5
c) completion	( " )	4	4	4	4	4
Product characteristics:						
a) hydroxyl value (mg of KOH/gram)		54.0	53.0	54.0	56.1	57.0
b) molecular weight		3120	3180	3120	3000	2950
c) ethylene oxide content		12%	14%	10%	14%	12%

### WHAT WE CLAIM IS:—

1. A process for the manufacture of a flexible polyurethane foam by reacting under foam-forming conditions an organic polyisocyanate reactant and an hydroxyl-containing reactant comprising or consisting of a polyether polyol which is a condensation product of an organic compound containing at least two replaceable hydrogen atoms in the molecule with ethylene oxide and propylene oxide, said polyol having an hydroxyl equivalent weight of at least 700 and the oxyethylene radical content thereof (expressed as ethylene oxide) being between 5 and 25% by weight of the total oxyethylene and oxypropylene radical content thereof (expressed as total ethylene oxide and propylene oxide), wherein said oxyethylene radicals are non-terminal radicals whereby said polyether polyol contains essen-

tially secondary hydroxyl groups in its molecular structure and said oxyethylene radicals are distributed in a random manner in a portion of the molecular structure of said polyol as the result of preparing said polyol by reacting said organic compound containing replaceable hydrogen atoms with a mixture of ethylene oxide and propylene oxide to form an intermediate adduct which is then reacted with propylene oxide only to form the required polyether polyol.

2. A process as claimed in claim 1, wherein said polyol is a condensation product of an organic polyhydroxy compound with ethylene oxide and propylene oxide.

3. A process as claimed in claim 2, wherein said polyhydroxy compound is glycerol.

4. A process as claimed in any one of the preceding claims, wherein the oxyethylene

radical content of said polyol is between 8 and 15% by weight.

5 5. A process as claimed in claim 4, wherein said oxyethylene radical content is between 10 and 14% by weight.

10 6. A process as claimed in any one of the preceding claims, wherein said polyol is formed by reacting glycerol with a mixture of 6 to 50% by weight of ethylene oxide and 50 to 94% by weight of propylene oxide and there-  
after reacting the resulting intermediate adduct with propylene oxide, the reactions being carried out in the presence of sodium hydroxide or potassium hydroxide as catalyst.

15 7. A process as claimed in any one of the preceding claims, wherein said polyurethane foam is produced by the one-shot method in which water is present as a co-reactant.

8. A process as claimed in claim 1 and

including any one or more of the process conditions and/or starting materials hereinbefore described. 20

9. A process for preparing a flexible polyurethane foam substantially as hereinbefore described with reference to Example I. 25

10. A flexible polyurethane foam manufactured by the process claimed in any one of the preceding claims.

11. A shaped article consisting of or comprising a polyurethane foam as claimed in claim 10. 30

WILLENS & ROBBINS,  
Chartered Patent Agents,  
Shell Centre,  
London, S.E.1.  
Agents for the Applicants.

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